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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1996-97		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Lewis Acid-Base Studies of Triorganogallium Compounds with Organophosphines				5. FUNDING NUMBERS Grant: N00014-96-1-0483 R&T Code: 4135002	
6. AUTHOR(S) O.T. Beachley, Jr. and John D. Maloney					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry State University of New York at Buffalo NSM Complex Buffalo, NY 14260-3000				8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 47	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000				10. SPONSORING/MONITORING AGENCY REPORT NUMBER n/a	
11. SUPPLEMENTARY NOTES Accepted for publication - Organometallics					
12a. DISTRIBUTION AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited. Reproduction in whole or in part is permitted for any purpose of the United States government.				12b. DISTRIBUTION CODE n/a	
13. ABSTRACT (Maximum 200 words) The relative Lewis acidities of a series of triorganogallium compounds GaR ₃ (R = Me, Et, CH ₂ CMe ₃ , CH ₂ SiMe ₃ , CH ₂ CMe ₂ Ph and C ₆ H ₂ Me ₃) toward a common Lewis base HPPH ₂ and the relative Lewis basicities of a series of organophosphines which incorporate an acidic hydrogen HP RR' (RR' = PPh ₂ , P(C ₆ H ₁₁) ₂ , PEt ₂ and P(H)(C ₆ H ₁₁)) toward a common Lewis acid Ga(CH ₂ CMe ₃) ₃ have been investigated and compared. Cryoscopic molecular weight data permitted an evaluation of the equilibrium constant for the dissociation of each of the adducts. The ³¹ P NMR spectral data which were consistent with the molecular weight data were also used to study the relative rates of hydrocarbon elimination reactions to form (R ₂ GaRR') ₂ .					
14. SUBJECT TERMS Organogallium-phosphorus adducts, Lewis acidity and basicity, elimination reactions				15. NUMBER OF PAGES 17	
				16. PRICE CODE n/a	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL		

OFFICE OF NAVAL RESEARCH

Contract N-00014-96-1-0483

R&T Code 4135002

TECHNICAL REPORT NO. 47

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Prepared for Publication

in

Organometallics

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12 June 1997

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Lewis Acid-Base Studies of Triorganogallium Compounds with Organophosphines

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ABSTRACT

The relative Lewis acidities of a series of triorganogallium compounds GaR_3 ($\text{R} = \text{Me}, \text{Et}, \text{CH}_2\text{CMe}_3, \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{CMe}_2\text{Ph}$ and $\text{C}_6\text{H}_2\text{Me}_3$) toward a common Lewis base HPPH_2 and the relative Lewis basicities of a series of organophosphines which incorporate an acidic hydrogen HPRR' ($\text{PRR}' = \text{PPh}_2, \text{P}(\text{C}_6\text{H}_{11})_2, \text{PEt}_2$ and $\text{P}(\text{H})(\text{C}_6\text{H}_{11})$) toward a common Lewis acid $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ have been investigated and compared. Cryoscopic molecular weight data permitted an evaluation of the equilibrium constant for the dissociation of each of the adducts. The ^{31}P NMR spectral data which were consistent with the molecular weight data were also used to study the relative rates of hydrocarbon elimination reactions to form $(\text{R}_2\text{GaPRR}')_2$.

Even though adducts are fundamental to the chemistry of the group 13 elements, suprisingly few investigations have focused on the characterization of the adducts of homoleptic triorganogallium compounds with phosphorus bases in order to understand if these compounds exist as single species in solution or whether they are partially dissociated or even fully dissociated in benzene solution. Only two of these types of adducts¹ $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ have been characterized in benzene solution by both cryoscopic molecular weight and NMR spectroscopic studies to our knowledge and both were found to be extensively dissociated in benzene solution. Of these two Lewis acids, $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ was the stronger acid toward HPPH_2 . The adduct $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ was a crystalline solid at room temperature and was characterized further by an X-ray structural study.¹ The other adduct $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ melted at 23.5 - 24.2 °C but was not characterized in the solid state. Four other adducts of homoleptic organogallium compounds $\text{Me}_3\text{Ga}\cdot\text{PMe}_3$ ², $\text{Me}_3\text{Ga}\cdot\text{PPh}_2\text{C}_2\text{H}_4\text{PPh}_2\cdot\text{GaMe}_3$ ³, $\text{Ph}_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ ⁴ and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ ⁵ have been structurally characterized but no data permitted a determination of the extent of dissociation of the first three of these adducts in solution. The last adduct $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$ ⁵ was investigated by ¹H and ¹³C NMR spectroscopy and was concluded to be undissociated in benzene solution.

The Lewis acidities of a series of triorganogallium(III) compounds GaR_3 ($\text{R} = \text{Me}$, Et , CH_2CMe_3 ¹, CH_2SiMe_3 ¹, $\text{CH}_2\text{CMe}_2\text{Ph}$ and $\text{C}_6\text{H}_2\text{Me}_3$) toward a common Lewis base HPPH_2 have been compared by using cryoscopic molecular weight data and ³¹P NMR spectroscopy. The cryoscopic molecular weight data for benzene solutions permitted calculations of the equilibrium constant for dissociation of the adduct (K_d , Equation 1) (Table 1), and the percent dissociation of the adduct (α) as a function of concentration, whereas ³¹P NMR spectral data (Table 2) were used to calculate changes in chemical shifts between that observed for the solution which contained the adduct and the solution of the pure phosphine ($\Delta\delta = [\delta(\text{R}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2) - \delta(\text{HPPH}_2)]$) and in coupling constants (¹J_{PH}) as

a function of concentration. All data confirm the existence of an equilibrium for each adduct (Equation 1) and are consistent with the following order of Lewis acidity toward



$HPPPh_2$, $GaMe_3$ (strongest acid) $> GaEt_3 \gg Ga(CH_2CMe_3)_3^1 > Ga(CH_2SiMe_3)_3^1 > Ga(CH_2CMe_2Ph)_3 \gg Ga(C_6H_2Me_3)_3$.

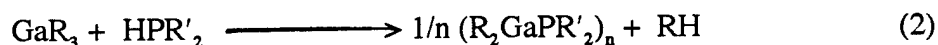
A comparison of the ^{31}P NMR spectroscopic data revealed significant differences between the chemical shifts and coupling constants of resonances for solutions of the adducts at the same concentration in comparison to the value observed for a solution of pure $HPPPh_2$. Furthermore, as the concentration of the adduct increased, the chemical shift of the observed ^{31}P NMR line moved downfield or away from the chemical shift of the line for pure $HPPPh_2$ in benzene solution ($\Delta\delta$ increased) as the coupling constant $^1J_{PH}$ increased (Table 2). Thus, the NMR and cryoscopic molecular weight data indicate that $Me_3Ga \cdot P(H)Ph_2$ and $Et_3Ga \cdot P(H)Ph_2$ are only slightly dissociated in benzene solution but $GaMe_3$ is a stronger Lewis acid than is $GaEt_3$ toward $HPPPh_2$. These observations may be correlated with the decreased steric effects of methyl groups. In contrast, the diphenylphosphine adducts of $Ga(CH_2CMe_3)_3^1$, $Ga(CH_2SiMe_3)_3^1$ and $Ga(CH_2CMe_2Ph)_3$ are significantly dissociated in solution with ≈ 0.05 m solutions being more than 50 % dissociated. Trimesitylgallium $Ga(C_6H_2Me_3)_3$ is so weak a Lewis acid that it does not appear to form significant concentrations of adduct even when the concentrations of the Lewis acid and base are 0.138 m, the highest concentrations studied.

The Lewis basicities of the phosphines $HPPPh_2^1$, $HP(C_6H_{11})_2$, $HPEt_2$ and $HP(H)(C_6H_{11})$ toward a common Lewis acid $Ga(CH_2CMe_3)_3$ were investigated. The cryoscopic molecular weight data was used to calculate an equilibrium constant for dissociation of each adduct (K_d , Equation 1) and the percent dissociation of the adduct (α) as a function of concentration. All data (Table 3) confirm the existence of an equilibrium

for each adduct and the following order of relative Lewis basicity for the phosphine, HPeEt_2 (strongest base) $> \text{HP}(\text{C}_6\text{H}_{11})_2 \approx \text{HP}(\text{H})(\text{C}_6\text{H}_{11}) > \text{HPPh}_2$. Thus, the least sterically demanding base HPeEt_2 is the strongest, as expected. The one surprise from our data is that $\text{HP}(\text{C}_6\text{H}_{11})_2$ and $\text{HP}(\text{H})(\text{C}_6\text{H}_{11})$ are of similar basicity.

The bulky dicyclohexylphosphine has an apparent base strength which is comparable to that of the less sterically demanding monocyclohexylphosphine. Since $\text{HP}(\text{H})(\text{C}_6\text{H}_{11})$ would have been expected to be more basic than $\text{HP}(\text{C}_6\text{H}_{11})_2$, steric effects cannot be the only important factor influencing the Lewis basicity of these two phosphines. One possible explanation for the observation of similar base strength of $\text{HP}(\text{C}_6\text{H}_{11})_2$ and of $\text{HP}(\text{H})(\text{C}_6\text{H}_{11})$ might be related to solvation effects. If the solvation of free $\text{HP}(\text{H})(\text{C}_6\text{H}_{11})$ is more favorable than is the solvation of the adduct, dissociation of the adduct would be favored. Molecular models suggest that the P-H protons in the adduct might be protected by the three neopentyl groups on gallium from an interaction with the pi-cloud of benzene whereas such hindrance would not occur for the free phosphine. It is also noteworthy that although $(\text{Me}_3\text{CCH}_2)_3\text{Ga} \cdot \text{P}(\text{H})(\text{C}_6\text{H}_{11})_2$ is significantly dissociated in benzene solution ($\sim 50\%$), the adduct has been isolated as a colorless crystalline solid with a sharp melting point ($42\text{--}43^\circ\text{C}$). A partial elemental (C/H) analysis of a sublimed sample was consistent with the empirical formula of the adduct. This observation is consistent with the existence of a pure, single compound in the solid state. It is regrettable that attempts to characterize this adduct in the solid state by an X-ray structural study were unsuccessful.

All of the phosphines used in these investigations have acidic protons with the potential to eliminate a hydrocarbon⁶ RH and form a phosphide of the type $(\text{R}_2\text{GaPR}'_2)_n$.



Available ^{31}P NMR spectral data were used to study the relative order of reactivity of different organogallium compounds with HPPh_2 and of different phosphines with

$\text{Ga}(\text{CH}_2\text{CMe}_3)_3$, all as benzene solutions of the same concentration. The following order for decreasing ease of elimination in benzene solution when the phosphine was HPPH_2 , GaEt_3 (most reactive) $>$ $\text{GaMe}_3 >$ $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3 \gg \text{Ga}(\text{CH}_2\text{CMe}_3)_3 \approx \text{Ga}(\text{C}_6\text{H}_2\text{Me}_3)_3$ (no reaction), was observed. It should be noted that this order is not the same order as was observed for the relative Lewis acidities toward HPPH_2 as the order for GaEt_3 and GaMe_3 are reversed. Both GaEt_3 and GaMe_3 eliminated an alkane and formed an organogallium phosphide $(\text{R}_2\text{GaPPh}_2)_n$ in benzene solution at room temperature but both reactions were very slow. The NMR data demonstrated that approximately 45 % of the $\text{Et}_3\text{Ga-P(H)Ph}_2$ as a 0.138 m solution was converted to $\text{Et}_2\text{GaPPh}_2$ after 12 d whereas a benzene solution of $\text{Me}_3\text{Ga-P(H)Ph}_2$ eliminated methane much more slowly. It is noteworthy that Robinson, Burns and Pennington⁷ described the use of a toluene (10 mL) solution of GaMe_3 (5 mmol) and HPPH_2 (5 mmol) to prepare $(\text{Me}_2\text{GaPPh}_2)_3$ for an X-ray structural study. When no solvent was used, temperatures of 90 - 110° C were reported by Coates and Graham⁸ to be necessary to initiate the elimination of methane from the adduct $\text{Me}_3\text{Ga}\cdot\text{P(H)Ph}_2$ in a sealed tube. When the elimination of SiMe_4 from a benzene solution of $(\text{Me}_3\text{SiCH}_2)_3\text{Ga-P(H)Ph}_2$ was investigated,^{1,9} heating to reflux was necessary to initiate a very slow reaction. In contrast, $(\text{Me}_3\text{CCH}_2)_3\text{Ga-P(H)Ph}_2$ did not eliminate CMe_4 , even upon refluxing a solution for 3 wk.^{1,10} Reactivity studies of $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ with $\text{HP(H)(C}_6\text{H}_{11})$ demonstrated that approximately 90 % of the CMe_4 was eliminated after a solution of $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ and $\text{HP(H)(C}_6\text{H}_{11})$ in benzene had been heated in a 70 °C oil bath for 7 d. However, heating for 18 d was necessary for complete reaction. The two phosphines $\text{HP(C}_6\text{H}_{11})_2$ and HPeEt_2 did not undergo elimination reactions with $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$, even upon heating benzene solutions at 70 °C for 3 wk.

These observations of the relative rates of elimination reactions in gallium phosphorus chemistry are consistent with the mechanism proposed for the elimination reaction in aluminum nitrogen chemistry.^{11,12} Kinetic studies for the $\text{HMe}_2\text{Al-N(H)(Me)(Ph)}$ system supported a bimolecular reaction between the Lewis acid and base.¹¹

Formation of the adduct was suggested to be a "dead-end path" for elimination.

Furthermore, studies of the $\text{HMe}_2\text{Al-N(H)}_2(\text{CH}_2\text{Ph})$ system¹² provided additional support for the conclusion that dissociation of the adduct was needed for the elimination reaction to occur. When $\text{HMe}_2\text{Al}\cdot\text{N(H)}_2(\text{CH}_2\text{Ph})$ was present as a solution in toluene, elimination of H_2 was observed. However, when the adduct precipitated from toluene solution, H_2 was not formed. The temperature was constant for these observations for the $\text{HMe}_2\text{Al-N(H)}_2(\text{CH}_2\text{Ph})$ system. Similarly, a benzene or toluene⁸ solution of $\text{Me}_3\text{Ga-P(H)Ph}_2$ eliminated methane at room temperature whereas the pure adduct without solvent⁷ required 90 - 110 °C. If the adduct had been the active species for elimination, the solution would have been expected to be less reactive. Second, the elimination of ethane from a benzene solution of $\text{Et}_3\text{Ga-P(H)Ph}_2$ was faster than was the elimination of methane from a solution of $\text{Me}_3\text{Ga-P(H)Ph}_2$ even though GaMe_3 is the stronger Lewis acid. Lastly, the extended times necessary for complete reactions for $\text{Et}_3\text{Ga-P(H)Ph}_2$ and $(\text{Me}_3\text{CCH}_2)_3\text{Ga-P(H)}_2(\text{C}_6\text{H}_{11})$ are also consistent with the occurrence of bimolecular reactions.

The observed reactivity patterns of GaMe_3 ¹³ and $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ ⁵ with $\text{P}(\text{SiMe}_3)_3$ also suggest that dissociation of these adducts might be required for the elimination of SiMe_4 with formation of $[\text{R}_2\text{GaP}(\text{SiMe}_3)_2]_n$. The reagents GaMe_3 and $\text{P}(\text{SiMe}_3)_3$ reacted smoothly in toluene solution to form $[\text{Me}_2\text{GaP}(\text{SiMe}_3)_2]_2$.¹³ In contrast, $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ reacted with $\text{P}(\text{SiMe}_3)_3$ in pentane solution to form only the adduct⁵ $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{SiMe}_3)_3$. ^1H and ^{13}C NMR spectra demonstrated that the adduct did not dissociate in benzene solution. The product of the elimination reaction $[(\text{Me}_3\text{SiCH}_2)_2\text{Ga}\cdot\text{P}(\text{SiMe}_3)_2]_2$ was not formed.⁵

Experimental Section

All compounds described in this section were extremely sensitive to oxygen and water and were manipulated in a standard vacuum line or under a purified argon atmosphere. The compounds $\text{Ga}(\text{CH}_2\text{CMe}_3)_3$ ¹⁴, $\text{Ga}(\text{CH}_2\text{SiMe}_3)_3$ ¹⁵, $\text{Ga}(\text{C}_6\text{H}_2\text{Me}_3)_3$ ¹⁶,

$\text{Ga}(\text{CH}_2\text{CMe}_2\text{Ph})_3$ ¹⁷, $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ ¹ and $(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ ¹ were prepared and purified by literature methods. Dicyclohexylphosphine, cyclohexylphosphine and diethylphosphine were purchased from Alfa Products whereas diphenylphosphine, trimethylgallium and triethylgallium were purchased from Strem Chemicals, Inc. All phosphines were purified by distillation prior to use. Solvents were dried by conventional procedures. Elemental analyses were performed by E + R Microanalytical Laboratory, Inc., Corona, NY. ¹H NMR spectra were recorded at 300 MHz by using a Varian Gemini-300 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to SiMe_4 at 0.00 ppm (δ) and C_6D_6 at 7.15 ppm. The ³¹P NMR spectra were recorded at 161.9 MHz by using a Varian VXR-400 spectrometer. Proton decoupled ³¹P NMR chemical shifts are referenced to 85 % H_3PO_4 at δ 0.00 ppm. All samples for NMR spectra were contained in tubes sealed by fusion of the glass. Melting points were observed in sealed capillaries and are uncorrected.

In a typical NMR spectroscopic study, the volatile component, either the phosphine or the triorganogallium compound, was vacuum distilled into a tared tube equipped with a Teflon valve and a standard tapered joint and weighed. Then, a stoichiometric quantity of the nonvolatile component and a known amount of C_6D_6 were placed into a reaction tube which was equipped with a magnetic stir bar and attached to an NMR tube and a Teflon valve adapter. After the volatile component was vacuum distilled into the reaction tube, the reaction mixture was stirred for 20 min at room temperature. The resulting solution was then poured into the NMR tube, the tube was cooled to -196 °C and flame sealed.

The adducts systems for cryoscopic molecular weight studies were prepared by using a procedure similar to that described previously for the NMR studies. Freezing point depressions were measured by using an instrument similar to that described by Shriver and Drezdson.¹⁸ Since the error typical of these types of measurements is approximately 10 %, the data in the experimental section for each compound give the actual calculated result,

whereas the corresponding value for K_d in the tables have been rounded off to one significant figure to avoid misinterpretation or over interpretation.

(Me₃CCH₂)₃Ga•P(H)Et₂. (a) ¹H NMR (0.0689 m, C₆D₆, δ): 0.75 (m, -CH₃), 0.92 (s, Ga-CH₂-), 1.18 (m, P-CH₂-), 1.21 (s, -CMe₃), 3.04 (dm, ¹J_{PH} = 273 Hz, -PH); (0.138 m, C₆D₆, δ): 0.76 (m, -CH₃), 0.91 (s, Ga-CH₂-), 1.18 (m, P-CH₂-), 1.21 (s, -CMe₃), 3.05 (dm, ¹J_{PH} = 273 Hz, -PH). ³¹P NMR (0.0689 m, C₆D₆, δ): -38.29 (dp, ¹J_{PH} = 271 Hz, ³J_{PCCH} = 13.4 Hz); (0.138 m, C₆D₆, δ): -37.87 (dp, ¹J_{PH} = 272 Hz, ³J_{PCCH} = 13.4 Hz). Cryoscopic molecular weight (measured upon mixing reagents), formula weight 373.1 (calcd m, obsd m, α or percent dissociation, K_d): 0.0541, 0.0584, 7.95 %, 3.71 x 10⁻⁴; 0.0460, 0.0507, 10.2 %, 5.35 x 10⁻⁴; 0.0376, 0.0422, 12.2 %, 6.41 x 10⁻⁴.
(b) A solution to study the elimination reaction was prepared by mixing 0.19 g (0.66 mmol) of Ga(CH₂CMe₃)₃, 0.060 g (0.67 mmol) of HPEt₂ and 4.82 g of C₆D₆. Initial spectrum, ³¹P NMR (0.14 m, 20 °C, δ): -37.87 (dp, ¹J_{PH} = 272 Hz, ³J_{PCCH} = 13.4 Hz, (Me₃CCH₂)₃Ga•P(H)Et₂). No change in the spectrum occurred after heating the sample for 3 wk at an oil bath temperature of 70 °C.

(Me₃CCH₂)₃Ga•P(H)₂(C₆H₁₁). (a) ¹H NMR (0.0689 m, C₆D₆, δ): 0.90 (s, -C₆H₁₁), 0.94 (s, -C₆H₁₁), 1.00 (s, -CMe₃), 1.07 (s, Ga-CH₂-), 1.12 (s, -CMe₃), 1.15 (s, -C₆H₁₁), 1.18 - 1.7 (br, C₆H₁₁), 2.75 (dm, ¹J_{PH} = 225 Hz, -PH); (0.138 m, C₆D₆, δ): 0.90 (s, -C₆H₁₁), 0.93 (s, -C₆H₁₁), 1.01 (s, -CMe₃), 1.06 (s, Ga-CH₂-), 1.10 (s, -CMe₃), 1.20 - 1.7 (br, -C₆H₁₁), 2.76 (dm, ¹J_{PH} = 225 Hz, -PH); ³¹P NMR (0.0689 m, C₆D₆, δ): -98.3 (t, ¹J_{PH} = 227 Hz); (0.138 m, C₆D₆, δ): -95.9 (t, ¹J_{PH} = 227 Hz). Cryoscopic molecular weight (measured upon mixing reagents), formula weight 399.3 (calcd m, obsd m, α or percent dissociation, K_d): 0.0552, 0.0828, 51.8 %, 2.76 x 10⁻²; 0.0430, 0.0663, 54.2 %, 2.76x 10⁻². **(b)** A solution to study the elimination reaction was prepared by using 0.10 g (0.36 mmol) of Ga(CH₂CMe₃)₃, 0.042 g (0.36 mmol) of H₂P(C₆H₁₁), and 2.69 g of C₆D₆. ³¹P NMR, initial spectrum, (0.13 m, 20 °C, δ): -95.9 (t, ¹J_{PH} = 227 Hz, (Me₃CCH₂)₃Ga•P(H)₂(C₆H₁₁)); 3 wk after mixing reagents: -63.63 (s, 3.9,

(Me_3CCH_2)₂GaP(H)(C₆H₁₁), -73.29 (s, 4.1, (Me_3CCH_2)₂GaP(H)(C₆H₁₁)), -105.3 (s, 1.0, (Me_3CCH_2)₃Ga•P(H)₂(C₆H₁₁)). A second solution was prepared by combining 0.13 g (0.47 mmol) of Ga(CH₂CMe₃)₃, 0.054 g (0.47 mmol) of H₂P(C₆H₁₁)₂, and 7.2 g of C₆D₆. ³¹P NMR, initial spectrum, (0.065 m, 20 °C, δ): -98.3 (t, ¹J_{PH} = 227 Hz, (Me_3CCH_2)₃Ga•P(H)₂(C₆H₁₁)); 7 d at 70 °C: -63.58 (s, 4.3, (Me_3CCH_2)₂GaP(H)(C₆H₁₁)), -73.27 (s, 5.3, , (Me_3CCH_2)₂GaP(H)(C₆H₁₁)), -104.8 (s, 1.0, (Me_3CCH_2)₃Ga•P(H)₂(C₆H₁₁)); 14 d at 70 °C: -63.83 (s, 5.3, (Me_3CCH_2)₂GaP(H)(C₆H₁₁)), -73.10 (s, 8.2, (Me_3CCH_2)₂GaP(H)(C₆H₁₁)), -107.3 (s, 1.0, , (Me_3CCH_2)₃Ga•P(H)₂(C₆H₁₁)); 18 d at 70 °C: -63.60 (s, 1.0, (Me_3CCH_2)₂GaP(H)(C₆H₁₁)), -73.31 (s, 1.2, (Me_3CCH_2)₂GaP(H)(C₆H₁₁)).

Synthesis of (Me_3CCH_2)₃Ga•P(H)(C₆H₁₁)₂. The reagents, 0.524 g (1.85 mmol) of Ga(CH₂CMe₃)₃ and 0.367 g (1.85 mmol) of HP(C₆H₁₁)₂, contained in screw-cap vials were transferred quantitatively to a Schlenk flask with repeated washing with dry pentane. After the solution was stirred for 2 h, the pentane was removed by vacuum distillation to leave a colorless solid which was purified by sublimation (0.995 g (Me_3CCH_2)₃Ga•P(H)(C₆H₁₁)₂, 1.69 mmol, 91.6 % yield). Mp 42 - 43 °C. ¹H NMR (0.0689 m, C₆D₆, δ): 0.82 (s, -C₆H₁₁), , 1.05 (s, Ga-CH₂-), 1.11 (s, -C₆H₁₁), 1.17 (s, -CMe₃), 1.37 (s, -C₆H₁₁), 1.54 (s, -C₆H₁₁), 1.60 (s, -C₆H₁₁), 1.73 (s, -C₆H₁₁), 2.98 (dt, ¹J_{PH} = 215 Hz, ²J_{HCH} = 5.3 Hz, -PH); (0.138 m, C₆D₆, δ): 0.90 (s, -C₆H₁₁), 1.00 (s, -C₆H₁₁), 1.07 (s, Ga-CH₂-), 1.08 (s, -C₆H₁₁), 1.14 (s, -C₆H₁₁), 1.20 (s, -CMe₃), 1.41 (s, -C₆H₁₁), 1.55 (s, -C₆H₁₁), 1.61 (s, -C₆H₁₁), 1.74 (s, -C₆H₁₁), 1.75 (s, -C₆H₁₁), 3.02 (dt, ¹J_{PH} = 231 Hz, , ²J_{HCH} = 4.5 Hz, -PH). ³¹P NMR (0.0689 m, C₆D₆, δ): -25.02 (d, ¹J_{PH} = 219 Hz); (0.138 m, C₆D₆, δ): -23.80 (d, ¹J_{PH} = 230 Hz). Anal. Calcd: C, 67.35; H, 11.72. Found: C, 67.27; 11.57. Cryoscopic molecular weight, formula weight 481.50 (calcd m, obsd m, α or percent dissociation, K_d): 0.0638, 0.0918, 43.8 %, 2.18 x 10⁻²; 0.0528, 0.0785, 48.8 %, 2.46 x 10⁻²; 0.0413, 0.0639, 54.6%, 2.71 x 10⁻². (b) Equal mol quantities of Ga(CH₂CMe₃)₃ and HP(C₆H₁₁)₂ were combined in C₆D₆ in order to test for

the occurrence of an elimination reaction. Initial ^{31}P NMR spectrum (0.14 m, 20 °C, δ): -25.02 (d, $^1J_{\text{PH}} = 219$ Hz, $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})(\text{C}_6\text{H}_{11})_2$). No change in the spectrum occurred after heating the sample for 3 wk at 70 °C.

$\text{Me}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$: ^1H NMR (0.0689 m, C_6D_6 , δ): 0.10 (s, $-\text{CH}_3$), 5.19 (d, $^1J_{\text{PH}} = 293$ Hz, $-\text{PH}$), 6.8-7.4 (m, Ph); (0.138 m, C_6D_6 , δ): 0.99 (s, $-\text{CH}_3$), 5.20 (d, $^1J_{\text{PH}} = 290$ Hz, $-\text{PH}$), 6.8-7.4 (m, Ph). ^{31}P NMR (0.0689 m, C_6D_6 , δ): -33.40 (dt, $^1J_{\text{PH}} = 290$ Hz, $^3J_{\text{PCCH}} = 9.0$ Hz). (0.138 m, C_6D_6 , δ): -33.17 (dp, $^1J_{\text{PH}} = 292$ Hz, $^3J_{\text{PCCH}} = 9.2$ Hz). Cryoscopic molecular weight (measured upon mixing reagents), formula weight 301.02 (calcd m, obsd m, α or percent dissociation, K_d): 0.0644, 0.0672, 4.34 %, 1.27×10^{-4} ; 0.0542, 0.0567, 4.61 %, 1.21×10^{-4} ; 0.0525, 0.0550, 4.76 %, 1.25×10^{-4} .

$\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$: ^1H NMR upon mixing reagents (0.0689 m, C_6D_6 , δ): 0.76 (s, $-\text{CH}_2-$), 1.41 (t, $^2J_{\text{HCH}} = 8.0$ Hz, $-\text{CH}_3$), 5.31 (d, $^1J_{\text{PH}} = 276$ Hz, $-\text{PH}$), 6.8-7.4 (m, Ph); (0.138 m, C_6D_6 , δ): 0.75 (s, $-\text{CH}_2-$), 1.40 (t, $^2J_{\text{HCH}} = 8.0$ Hz, $-\text{CH}_3$), 5.31 (d, $^1J_{\text{PH}} = 294$ Hz, $-\text{PH}$), 6.8-7.4 (m, Ph); ^{31}P NMR (1 h after mixing reagents; 0.0689 m, C_6D_6 , δ): -35.84 (dp, $^1J_{\text{PH}} = 272$ Hz, $^3J_{\text{PCCH}} = 9.4$ Hz), 4.3, $\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$), -46.32 (s, 1.0, $\text{Et}_2\text{Ga}\cdot\text{PPh}_2$); (1 h after mixing reagents; 0.138 m, C_6D_6 , δ): -34.00 (dp, $^1J_{\text{PH}} = 296$ Hz, $^3J_{\text{PCCH}} = 9.4$ Hz, 4.4, $\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$), -46.33 (s, 1.0, $\text{Et}_2\text{Ga}\cdot\text{PPh}_2$); (3 d after mixing reagents; 0.0689 m, C_6D_6 , δ): -35.83 (dp, $^1J_{\text{PH}} = 272$ Hz, $^3J_{\text{PCCH}} = 8.4$ Hz, 3.9, $\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$), -46.24 (s, 1.0, $\text{Et}_2\text{Ga}\cdot\text{PPh}_2$); (3 d after mixing reagents, 0.138 m, C_6D_6 , δ): -33.98 (dp, $^1J_{\text{PH}} = 294$ Hz, $^3J_{\text{PCCH}} = 9.6$ Hz, 2.7, $\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$), -46.23 (s, 1.0, $\text{Et}_2\text{Ga}\cdot\text{PPh}_2$); (12 d after mixing reagents, 0.0689 m, C_6D_6 , δ): -36.05 (dp, $^1J_{\text{PH}} = 278$ Hz, $^3J_{\text{PCCH}} = 8.0$ Hz, 2.6, $\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$), -46.39 (s, 1.0, $\text{Et}_2\text{Ga}\cdot\text{PPh}_2$); (12 d after mixing reagents, 0.138 m, C_6D_6 , δ): -34.14 (dp, $^1J_{\text{PH}} = 295$ Hz, $^3J_{\text{PCCH}} = 9.1$ Hz, 1.2, $\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$), -46.39 (s, 1.0, $\text{Et}_2\text{Ga}\cdot\text{PPh}_2$). Cryoscopic molecular weight (measured upon mixing reagents), formula weight 343.10 (calcd m, obsd m, α or percent dissociation, K_d): 0.0720, 0.0785, 9.03 %, 6.45×10^{-4} ; 0.0580, 0.0649, 11.9 %, 9.32×10^{-4} ; 0.0422, 0.0478, 13.3 %, 8.57×10^{-4} .

(PhMe₂CCH₂)₃Ga•P(H)Ph₂. ¹H NMR (0.0689 m, C₆D₆, δ): 0.83 (s, Ga-CH₂-), 1.23 (s, -CMe₂-), 5.15 (d, ¹J_{PH} = 219 Hz, -PH) 6.80-7.40 (m, Ph); (0.138 m, C₆D₆, δ): 0.84 (s, Ga-CH₂-), 1.24 (s, -CMe₂-), 5.13 (d, ¹J_{PH} = 231 Hz, -PH), 6.82-7.42 (m, Ph). ³¹P NMR (0.0689 m, C₆D₆, δ): -39.17 (dp, ¹J_{PH} = 224 Hz, ³J_{PCCH} = 7.3 Hz); (0.138 m, C₆D₆, δ): -38.40 (dp, ¹J_{PH} = 230 Hz, ³J_{PCCH} = 7.4 Hz). Cryoscopic molecular weight, formula weight 655.56 (calcd m, obsd m, α or percent dissociation, K_d): 0.0495, 0.0823, 66.3 %, 6.44 x 10⁻²; 0.0414, 0.0690, 66.7 %, 5.52 x 10⁻²; 0.0315, 0.0518, 64.4%, 3.68 x 10⁻².

Reaction of Ga(C₆H₂Me₃)₃ with HPPH₂. ¹H NMR (0.0689 m of each reagent, C₆D₆, δ): 2.13 (s, p-Me), 2.32 (s, o-Me), 5.17 (d, ¹J_{PH} = 216 Hz, -PH), 6.73 (s, m-H), 6.9-7.4 (m, Ph). (0.138 m, C₆D₆, δ): 2.13 (s, p-Me), 2.32 (s, o-Me), 5.17 (d, ¹J_{PH} = 216 Hz, -PH), 6.73 (s, m-H), 6.9-7.4 (m, Ph). ³¹P NMR (0.0689 m, C₆D₆, δ): -40.40 (dp, ¹J_{PH} = 217 Hz, ³J_{PCCH} = 6.9 Hz); (0.138 m, C₆D₆, δ): -40.40 (dp, ¹J_{PH} = 217 Hz, ³J_{PCCH} = 7.6 Hz). Cryoscopic molecular weight, formula weight 613.46 (calcd m, obsd m, α or percent dissociation): 0.0415, 0.0832, 100 %; 0.0371, 0.0739, 99.2 %.

Acknowledgements. This work was supported in part by the Office of Naval Research. We thank Matthew J. Noble for preparing the Ga(CH₂CMe₂Ph)₃ which was used in this study.

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Table 1. Cryoscopic Molecular Weight Studies of $R_3Ga \cdot P(H)Ph_2$ Adduct Systems in Benzene Solution.

Adduct System	Calcd.(m)	Obsd. (m)	α	K_d (Ave)
$Me_3Ga \cdot P(H)Ph_2$	0.0644	0.0672	4.3	1×10^{-4}
	0.0525	0.0550	4.8	
$Et_3Ga \cdot P(H)Ph_2$	0.0580	0.0649	12	8×10^{-4}
	0.0422	0.0478	13	
$(Me_3CCH_2)_3Ga \cdot P(H)Ph_2^1$	0.0522	0.0828	58	4×10^{-2}
	0.0415	0.0668	61	
$(Me_3SiCH_2)_3Ga \cdot P(H)Ph_2^1$	0.0492	0.0794	62	5×10^{-2}
	0.0376	0.0629	67	
$(PhMe_2CCH_2)_3Ga \cdot P(H)Ph_2$	0.0495	0.0823	66	5×10^{-2}
	0.0371	0.0690	67	
$(C_6H_2Me_3)_3Ga \cdot P(H)Ph_2$	0.0415	0.0832	100	----
	0.0371	0.739	99	

Table 2. ^{31}P NMR Spectral Data for $\text{R}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$ Adduct Systems in Benzene Solution.

Adduct System	Conc.(m)	δ (ppm)	$\Delta\delta$ (ppm)	$^1J_{\text{PH}}$ (Hz)
PPh_2H	---	-40.40	---	215
$\text{Me}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$	0.0689	-33.40	7.00	290
	0.138	-33.17	7.23	292
$\text{Et}_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$	0.0689	-35.84	4.56	272
	0.138	-34.00	6.40	296
$(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2^1$	0.0689	-37.83	2.57	232
	0.138	-36.48	3.92	241
$(\text{Me}_3\text{SiCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2^1$	0.0689	-38.45	1.95	232
	0.138	-37.74	2.66	240
$(\text{PhMe}_2\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$	0.689	-39.17	1.23	224
	0.138	-38.40	2.00	230
$(\text{C}_6\text{H}_2\text{Me}_3)_3\text{Ga}\cdot\text{P}(\text{H})\text{Ph}_2$	0.0689	-40.40	0.00	217
	0.138	-40.40	0.00	217

**Table 3. Cryoscopic Molecular Weight Studies for
(Me₃CCH₂)₃Ga•P(H)RR' Adduct Systems in Benzene Solution.**

Adduct System	Calcd.(m)	Obsd. (m)	α	$K_d(\text{Ave})$
(Me ₃ CCH ₂) ₃ Ga•P(H)Et ₂	0.0541	0.0584	7.9	5×10^{-4}
	0.0460	0.0507	10	
(Me ₃ CCH ₂) ₃ Ga•P(H)(C ₆ H ₁₁) ₂	0.0526	0.0785	49	2×10^{-2}
	0.0413	0.0639	55	
(Me ₃ CCH ₂) ₃ Ga•P(H) ₂ (C ₆ H ₁₁)	0.0552	0.0828	52	3×10^{-2}
	0.0430	0.0663	54	
(Me ₃ CCH ₂) ₃ Ga•P(H)Ph ₂ ¹	0.0522	0.0828	58	4×10^{-2}
	0.0415	0.0668	61	

Table 4. ^{31}P NMR Spectral Data for $(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{RR}$ Adduct Systems in Benzene Solution.

Compound	Conc.(m)	δ (ppm)	$\Delta\delta$ (ppm)	$^1J_{\text{PH}}$ (Hz)
PEt_2H	---	-55.13	---	192
$(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})\text{Et}_2$	0.0689	-38.29	16.84	271
	0.138	-37.87	17.26	272
$\text{P}(\text{C}_6\text{H}_{11})_2\text{H}$	---	-27.40	---	193
$(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})(\text{C}_6\text{H}_{11})_2$	0.0689	-25.02	2.38	219
	0.138	-25.80	3.60	230
$\text{P}(\text{C}_6\text{H}_{11})_2\text{H}_2$	---	-111.4	---	189
$(\text{Me}_3\text{CCH}_2)_3\text{Ga}\cdot\text{P}(\text{H})_2(\text{C}_6\text{H}_{11})$	0.0689	-98.3	13.1	226
	0.138	-95.9	15.5	227

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